Molecules on Ice

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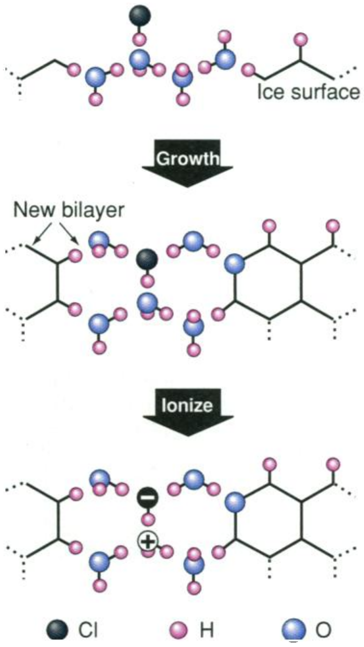

Mechanism for HCl sticking and ionizing on ice.

The ozone hole that forms in the spring months over the Antarctic is thought to be produced through a network of chemical reactions catalyzed by the surfaces of ice crystals in polar stratospheric clouds (PSCs). A reaction between chlorine reservoir molecules, such as $HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$, is kinetically forbidden in the gas phase but proceeds quickly on the surface of ice and produces Cl_2 molecules that are photodissociated by sunlight to yield the Cl atoms that destroy ozone. This destructive chain of events begins when HCl molecules stick to the ice crystals, and the mechanism for this crucial sticking process has been the subject of much debate. On page 1563 of this issue, Gertner and Hynes describe a mechanism that explains how HCl sticks to ice (*1*).

Such chemical processes have been the subject of intensive study ever since the Antarctic ozone hole was discovered in 1985 by a group from the British Antarctic Survey (*2*). It was soon realized that the properties of PSCs were important (*3*), which stimulated a whole new field of laboratory-based work, relevant to atmospheric chemistry, concerning heterogeneous reactions on surfaces or in liquid droplets. Indeed, some of the leading groups that had previously been concerned with measuring the rates of gas-phase chemical reactions important in the atmosphere immediately turned their attention to the problems of reactions on surfaces such as ice, including the group of Molina, who, with Rowland and Crutzen, was awarded the 1995 Nobel Prize in Chemistry for his work on the chemistry of the Earth's atmosphere. However, direct measurements on the rates and mechanisms of these heterogeneous reactions are hard to carry out under the conditions of the Antarctic stratosphere: The reaction network is complex, not much is known about PSCs, and temperatures can be as low as 190 K. For these reasons, computer simulations, such as the one carried out by Gertner and Hynes (*1*), are very useful.

Computer simulations of HCl sticking to ice were first carried out in 1992 at Cambridge University (*4*), and in this work the classical equations of motion for rigid HCl molecules interacting with a prepared ice surface at 190 K were solved. It was found that an HCl molecule did stick to the ice for about 10^{-7} s but then desorbed. This is not sufficient time for the HCl to react with species such as $ClONO_2$. The model contradicted experimental studies of the sticking process that showed a high coverage of HCl on the surface of ice (*5*). In addition, the model did not allow the HCl to dissociate into ions on the ice surface: Although the weakly bound dimer $HCl.H_2O$ is purely covalent, it is well known that HCl dissolves in water to form ions. Therefore, it is important to know if the water molecules on the surface of ice at 190 K have enough mobility to solvate HCl to produce H_3O^+ and Cl^- before the HCl has time to desorb from the surface. Infrared spectroscopy measurements on ice exposed to HCl show bands associated with H_3O^+ (*6*), and a simple computer model suggests that the dissociation of HCl into ions might be feasible thermodynamically (*7*). However, the detailed reaction mechanism for this process remained a puzzle.

A key experiment was carried out at the University of Colorado in Boulder by George and co-workers (*8*). They developed an optical interference experiment to study the surface of ice under stratospheric conditions and discovered that it has a strongly dynamic character, with water molecules continually evaporating from and condensing on the surface. This dynamic character was exploited in the computer model that Gertner and Hynes developed in the same department in Boulder. Their technique is adapted from a sophisticated simulation method that this group successfully used before to model the ionization of hydrogen halides in liquid water (*9*). They argue that collisions of water molecules with HCl temporarily stuck on the ice surface trap the HCl; they find enough water molecules can then surround the HCl so that it can ionize efficiently (see figure). This model does not require the ice surface to have a quasi-liquid layer initially, but the dynamic nature of the ice surface is crucial.

The molecular dynamics model used by Gertner and Hynes contains several simplifications (such as the neglect of surface defects), and ice crystals of nitric acid trihydrate, highly abundant in polar stratospheric clouds, were not treated. However, their model does provide a simple and plausible mechanism for explaining why ionic and not molecular mechanisms occur in the key reactions on ice crystals in PSCs that lead to ozone depletion. Can other molecules also be subject to the same mechanism? If, for example, HF could be trapped and ionized in this way, the implications would be enormous, as it is commonly thought that HF is inert in the reaction networks involved in the destruction of ozone. A thermodynamic model suggests that it will be hard to ionize HF on ice (*7*), but if the ionization process occurs for HCl, then HBr and HI will be very likely candidates for the same mechanism.

The need for considering surface reactions in stratospheric chemistry has opened up an area of surface science that has previously had little attention. It has been necessary to develop and apply novel experimental techniques and new computational methods. This is a good example of how a rather applied problem can stimulate quite basic research in the laboratory and on the computer.

References

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